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From chemical disinfection to electrodisinfection: The obligatory itinerary?

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ABSTRACT

This review concerns chemical disinfection and electrodisinfection (ED). Chemical disinfection is a common unit process used in water supply and wastewater treatment. Traditionally, chlorination is the most dominant method of disinfection. However, there are serious safety concerns and great ecological risks involved in the use of chlorine. Other methods, such as ozonation, UV radiation and ClO_2 application, are still more expensive or less convenient than chlorination. It has been reported that ED can destroy a wide variety of microorganisms from viruses through bacteria and algae to larger species, such as *Euglena*. The ED process has the potential to be developed as a robust, cost-effective and environmental friendly alternative of disinfection, particularly for saline sewage effluent and for seawater in cooling and other industrial usages. During ED, water is forced through a disinfector that is equipped with electrodes on which current is charged. This practice is different from conventional electro-chlorination (E-C), which relies on the production of a concentrated chlorine solution by electrolysing a side-stream of salt water. A number of theories have been proposed to explain ED's major bactericidal actions, including E-C, destruction caused by the electric field, and generation of energy rich but short-lived intermediate ED products. Increasing attention has been recently given to free radicals, such as $^{\bullet}OH^-$ and $O_2^{\bullet -}$, that could be produced during electrolysis, for their possible role in ED's strong killing actions, although more evidence remain to be collected. On the other hand, ED has many advantages compared with chemical disinfection. ED reliability has been proven in several practical applications, mainly for the disinfection of drinking water, swimming pool water and industrial cooling water. ED has also been used or tested for the reduction of bacterial contamination in dental water supplies, and for the disinfection of contact lenses and ion exchange resins, etc. However, only a few ED products are currently available in the market. This is due to the relative unfamiliarity of the technology, and fierce market competition with other technologies. Eventually, the cost and performance advantages of ED should lead to its wider use. Finally, electrocoagulation (EC) as an efficient process in mineral and organic matters removal has been also proven efficient in microorganisms removal; hence, this electrochemical process may be presented as promising water/wastewater treatment technology.

***Keywords*:** Drinking water; Disinfection; Electrodisinfection; Electro-chlorination; Electrocoagulation; Disinfection by-products

1. Introduction

Drinking water disinfection typically includes multibarrier water treatment processes such as physical processes (settlement, sand and membrane filtration) [1], chemical processes (chlorination, ozonation) [2] and as well as physico-chemical processes (coagulation/flocculation) [3–5]. Disinfection by membrane separation is considered as an effective technology and finds more and more applications

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in drinking water and wastewater treatment [6]. Indeed, in contrast to the conventional methods, the membrane method has particular advantages [7] such as complete disinfection which is generally achieved by a microfiltration membrane having 0.1 µm pore size [7] and the chemical composition of water is not affected by using the disinfection procedure. The membrane system also has some disadvantages such as decrease in membrane performance due to plugging and fouling [8] which is unavoidable in almost any membrane use process and some pre-treatment operations and regular cleaning of the membrane are necessary to maintain its performance constant [9].

Disinfection processes have two main purposes: primary disinfection for removal or inactivation of microbiological contaminants in the raw water supply and the provision of a residual in the distribution network. Disinfection [10] of water can be traced back to ca. 2000 BC to ancient Sanskrit writings that prescribed that water should be exposed to sunlight and filtered through charcoal and that "foul water" be treated by boiling and "by dipping seven times into a piece of hot copper and then filtering it. Other very early references to boiling water and storage in silver flagons and other containers exist as are ancient efforts of water disinfection based on the use of copper, silver and electrolysis. The first U.S. patent on chlorination of water dates back to May 22, 1898, and was awarded to Albert R. Lieds. The low cost and high potency of chlorine [2,11] as a water disinfectant promoted its usage since the mid-18th century. However, the practice of continuous addition was not initiated until the early 1900s and it is still the main water disinfectant used throughout the world [12].

Electrodisinfection (ED) can be defined as the eradication of microorganisms by using an electric current passed through the water [2] under treatment (Fig. 1) by means of suitable electrodes [13]. At the phase boundary between the electrodes and the water, the electric current leads to the electrochemical production of disinfecting species [14] from the water itself (for example, ozone), or from species dissolved in the water (for example, chloride is oxidised to free chlorine) [15].

Attempts to clean or disinfect water by direct electrolysis had been reported as early as the nineteenth century [15]. It has even been speculated that the electrical elements (the so-called 'Baghdad battery'), which were discovered in 1936 in the ruins of a Parthian city (inhabited from about 300 BC to 300 AD) near Baghdad in Iraq, were in use for the electrochemical preparation of germ-free water [15]. Since the end of the nineteenth century there have been frequent attempts to use ED. Until recently none have been successful, at least not for long-term practical use.

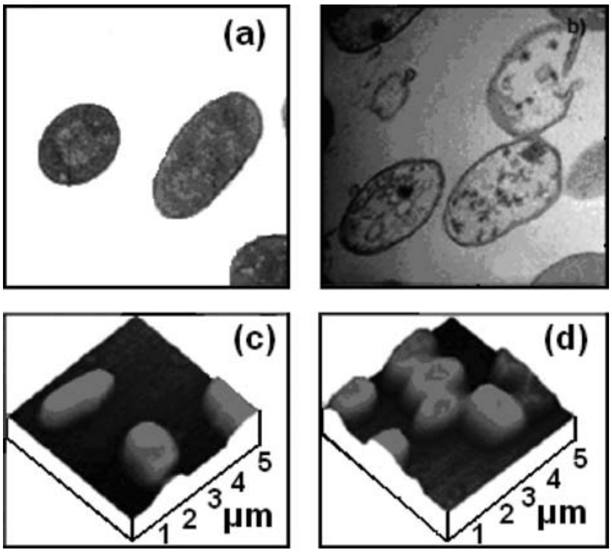

Fig. 1. Morphological changes in *E. coli* cells resulting from electrolysis at 100 mA cm^{-2} for 5 min using a Nb/BDD anode. [*E. coli*]$_0$ = 108 colony-forming units (CFU) mL^{-1}, $[KH_2PO4]_0$ = 0.2 M, pH 7.1, 25°C. Transmission electron microscopy (TEM) images before (a) and after (b) electrolysis; atomic force microscopy (AFM) images before (c) and after (d) electrolysis [2].

Different terms are or have been in use to describe this type of water treatment process or the water sproduced by this process, such as 'electrolytic disinfection', 'electrochemical disinfection', 'anodic oxidation', 'functional water' and 'electrochemically activated water' among others [15].

A distinction must be made here between disinfection [16] and sterilisation procedures. *Disinfection* relates to the killing of disease-related organisms, whereas *sterilisation* involves the killing of all organisms present [12].

The promulgation of a number of new regulations for the control of microbiological and chemical pollutants in drinking water [17] has prompted the search for suitable, cost-effective alternative methods for primary disinfection [18]. Of particular concern are the disinfection by-products (DBPs) of chlorination [19] and that groundwaters high in natural organic matter (NOM) may be incompatible with the more traditional chemical disinfectants [20,21]. Even the alternatives currently considered such as chloramines may be inappropriate because they are weak virucides and would be unlikely to meet primary disinfection requirements [12].

We shall discuss electrochemical technologies (ET) for water disinfection in this review.

2. Water disinfection: background and principles

2.1. General considerations

The methods for water disinfection may be classified as follows:

- **Chemical action:** A variety of chemical agents can be used to inactivate microorganisms. These include halogens and derivatives ($C1_2$, Br_2, I_2, HOCl, OCI^- ClO_2, HOBr, HOI, polyiodide anion exchange resins, etc.), oxygenated and highly oxidising compounds (ozone, hydrogen peroxide, phenols, alcohols, persulfate and percarbonate, peracetic acid, potassium permanganate, etc.), metal ions (Ag^+, Cu^{2+}, etc.), dyes, quaternary ammonium compounds, strong acids and bases, and enzymes.
- Physical action: Electromagnetic radiation (ultrasonic waves, heat, visible light, UV light, gamma radiation, X-rays), particle radiation (electron beam), and electrical current [12].

The mechanisms for microbial inactivation include the following:

- Laceration of the cell wall,
- Modification of cell permeability,
- Modification of the nature of the protoplasm,
- Alteration of nucleic acids,
- Disruption of protein synthesis,
- Induction of abnormal redox processes,
- Inhibition of enzyme activity [12,22].

A variety of factors influence the disinfection efficiency, including the contact time, chemical nature, and concentration of the disinfecting agent as well as the initial mixing mode and point of injection, nature and intensity of the physical agents, temperature, type, concentration and age of the microorganisms, and the nature of the liquid carrier. We shall explore a few of these in the sections that follow [12].

2.2. Chemical disinfection

Common attributes of the important chemical disinfectants (Cl_2, OCI^-, ClO_2, and O_3) are the following:

- Highly potent microorganism inactiv ation and relatively high toxicity to humans and animals.
- Active interaction (normally oxidation or addition) with organic matter (OM) and with inorganic reducing agents [23].
- Sufficient solubility in aqueous media (except the dihalogens due to their nonpolar nature).
- Penetration capability through surfaces and cell membranes.
- Moderate to good deodorising ability [12].

The relative stabilities of these chemicals follow the order $Cl_2 > OCl^- > ClO_2$, O_3, and their relative costs are $O_3 > ClO_2$, $OCl^- > Cl_2$. Undesirable characteristics include DBP production, corrosivity to metallic materials, membrane attack, and discoloration of dyes and tints. In fact, it has been stated that it would be ideal to *separate* the oxidation and disinfection functions in the water treatment system. In this regard, it is worth noting that another major realm of use of these chemicals is in the pulp and paper industry [12].

2.3. Disinfection by-products

Drinking water disinfection is vital for preventing the spread of diseases caused by waterborne pathogens. However, chemical disinfectants can also form by-products with potential health concerns [24]. Chlorine reacts with NOM to produce halogenated DBPs. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two most prevalent groups among known specific DBPs formed during chlorination [25] of natural waters [26]. Because of concerns over the effect that these DBPs might have on human health, the US Environmental Protection Agency (USEPA) has set stringent regulatory limits for four THMs and five HAAs [27]. In response to the these regulations, a great deal of effort has been made by drinking water utilities in evaluating alternative disinfectants, such as chloramines, ozone and chlorine dioxide, to lower the concentrations of these two groups of regulated DBPs [28].

There has been an increasing interest in using chloramines as a secondary disinfectant for maintaining a residual throughout the distribution system [29]. Chloramines form only trace amounts of THMs and trihalogenated HAAs (THAAs). However, the formation of dihalogenated HAAs (DHAAs) and total organic halogen (TOX), although generally lower than that from chlorination, can still reach significant levels depending on the dose, chlorine to ammonia ratio, pH and other conditions [30]. It has been shown that more than 70% of the TOX formed by chloramines cannot be attributed to known specific DBPs. This value is higher than that from chlorination where approximately 50% of the TOX remains unknown. Although TOX concentrations are not currently regulated, they do represent the total amount of halogenated organic by-products produced. Researchers [28] have noted that the regulated by-products cannot account for observed toxicity (both level and target organs) from epidemiological studies of drinking water consumption. The non-regulated TOX, here referred to as the ‘‘unknown TOX (UTOX)’’, may contain a substantial amount of toxicologically important compounds [28].

Ozone is a potent oxidant and disinfectant that decomposes quickly in drinking water. Because of its instability, ozone cannot produce a persistent disinfectant residual in distribution systems [26]. Chlorine or chloramines have been used in conjunction with ozone for this purpose. Therefore, there has also been a longstanding interest in the impact that ozone might have on DBP precursors. Both increases and decreases in DBP formation from chlorination or chloramination following preozonation have been observed. These increases and decreases depend on the DBP precursors and disinfection conditions used in the process [31–33]. Most researchers reported a decrease of THMs, HAAs and TOX upon chlorination [34] of natural waters as a result of preozonation [28].

Similar to ozone, chlorine dioxide is also a powerful disinfectant and oxidant. Typically, about 70% of the applied chlorine dioxide is ultimately reduced to chlorite [26,35]. The USEPA has set a maximum contaminant level (MCL) for chlorite at 1.0 mg L^{-1}. Thus, the chlorine dioxide dose should not exceed about 1.4 mg L^{-1} to ensure that the chlorite limit is met. Halogenated organic by-products formed by chlorine dioxide are largely unknown. Limited studies have shown that chlorine dioxide does not produce THMs and THAAs to a significant extent. However, it does produce appreciable amounts of DHAAs and TOX during drinking water treatment [28,35–36].

3. Electrodisinfection of water

3.1 Introduction

Common disinfection techniques used in water treatment include chlorination, ozonation and UV irradiation. Chlorination is still a common technique but unfortunately some species of bacteria have the ability to mutate under the adverse conditions of chlorination. This results in the production of strains that are more tolerant to normal chlorine treatment levels. To combat this it is possible to use higher chlorine levels, but such treatment can result in unpleasant flavours and odours (due to the formation of chlorophenols and other halocarbons) [37].

As with the organic pollutants [38], microorganisms can be electrochemically inactivated [39,40] either directly or via the generation of "killer" agents such as $^{\bullet}OH$. A third route involves the electrosorption of bacteria and the like on the electrode surface [41] and their subsequent inactivation. Again, as with their organic counterparts, the direct and indirect routes are not always distinguishable; and it is possible that, in many of the studies done to date, both processes play a significant role [12].

Electrode materials [42] vary widely, depending on the disinfecting agent desired. Cathode materials [43] include stainless steel, copper, graphite, carbon cloth and reticulated vitreous carbon (RVC). Anode materials include platinised titanium or niobium, tantalum, graphite, carbon, metal oxides, silver, copper, nickel, monel, dimensionally stable anodes (DSA) and combinations thereof. Electrocatalytic materials can be incorporated into electrodes, for example, in the form of coatings, or incorporated into cell separators. Three-dimensional electrodes [44] have also been successfully used. Narrow gap cell technology involving the use of a solid polymer electrolyte (SPE) has been applied to electrochemical water disinfection to decrease cell resistance and avoid the need for adding supporting electrolytes. Examples of the present application include chlorine and hypochlorite production. Direct as well as low and high frequency alternating current (AC) have been used for disinfection purposes. Deposit formation may occur on the cathodes, particularly in the case of hard water. This problem has been prevented by periodic current reversal and producing oscillations of the electrode. Treatment with direct current (DC) or AC has been shown to inactivate a large variety of microorganisms including viruses, bacteria, algae, coliforms [39], fecal streptococci and relatively large species such as *Euglena* [12].

3.2. Electrosorption of microorganisms and direct electron transfer

Bacteria show a tendency to adsorb onto surfaces such as activated carbon, fibrous carbon or ion exchange resins. This tendency is driven mainly by electrostatic forces between charged groups on the cell wall (e.g., amino and carboxylic groups) and on the adsorbent. For example, Gram-negative bacilli concentration was reduced by some five orders of magnitude upon adsorption on activated charcoal [12].

The potential-induced adsorption of solutes onto the surface of an electrode [45] is called *electrosorption,* and its effectiveness depends on the potential of zero charge of the adsorbate. (This is also the principle used in the removal of suspended solids by electrofiltration.) For example, the application of an external potential (positive with respect to the potential of zero charge of the adsorbate) to a carbon felt electrode promoted a reduction in the concentration [46] of *Escherichia coli (E. coli)* in the suspension passing through the electrode by three or four orders of magnitude. A major reduction *in S. typhimurium* concentration was also observed. Interestingly, this method is not effective for microorganism *inactivation* since part of the bacteria can be released back to the suspension [12].

Even though this phenomenon does not strictly fall within the framework of the definition of *disinfection* given at the beginning of this review, it does remove *disease-related* microorganisms and thus can be an effective method for the prevention of infection-related problems. Additional advantages are that chemicals need not be added to the suspension for treatment, the adsorbent can be at least partially regenerated, dead microorganisms do not remain in the treated water, and inexpensive adsorbents can be used. An interesting alternative consist of the adsorption of bactericides onto the electrode. The applicability of the DC electrosorption approach to nonbacterial pathogens (e.g., viruses, protozoan cysts), however, remains to be established [12].

An interesting electrochemical disinfection (ED) [47] process has been described based on AC perturbation of the electrode/electrolyte interface. In the anodic part of the cycle, the pathogen adsorbed on the electrode is oxidised. In the cathodic portion, the oxidation products are reductively removed from the electrode surface and a clean electrode surface is regenerated for subsequent disinfection cycles. This system is reported to work not only on bacteria but on larger organisms such as protozoa [12].

Possible electrocution mechanisms involve the induction of abnormal redox processes or even forced (unnatural) electro-osmotic flow at the cellular level because of the current flow. Direct electrochemical oxidation of intercellular coenzyme A has been claimed for the inactivation of bacteria at electrode surfaces. This method is claimed to also reduce microbial fouling of the electrode [42] and other surfaces. Carbon anodes were used in early work. This approach has since been extended to the use of large surface area graphite-silicone and carbon-chloroprene electrode surfaces [12].

An important application of the “direct” oxidation approach is prevention of marine biofouling of structures such as water-cooling pipes and ship hulls. The accumulation of biomass on these surfaces causes increased fluid frictional resistance in the case of ship hulls and decreased heat-transfer efficiency for cooling pipes. The use of toxic chemical agents such as copper and organotin is not environmentally safe because of leaching of these species from the surfaces to be protected [12].

3.3. Electrodisinfection’s mechanisms

The inactivation of bacteria (and yeast cells) by electrochemical means has been well documented [39,48]. Several mechanisms have been proposed to account for the lethality of electrochemical exposure, including oxidative stress and cell death due to electrochemically generated oxidants, irreversible permeabilisation of cell membranes by the applied electric field (EF), and electrochemical oxidation of vital cellular constituents during exposure to electric current or induced EFs [49].

Chemical oxidants are generated when electric current is applied to aqueous suspensions of microbes with immersed electrodes [39]. Electrolysis at the electrodes generates a variety of oxidants in the presence of oxygen, including hydrogen peroxide and ozone, as well as free chlorine and chlorine dioxide when chloride ions are present in the solution [39]. Such oxidants are responsible for most, but not all, of the lethality of the applied direct current. Current research indicates that antimicrobial agents and electric current act synergistically to inactivate microbes [49].

EFs are themselves harmful to cells [39]. It has been shown that this is primarily due to the irreversible permeabilisation of the cell membrane [50]. Experiments conducted on artificial bilayer lipid membranes indicate that a membrane exposed to an external EF gathers charge much like a capacitor, and a transmembrane potential is induced. A short-lived steady-state current across the membrane is established when the membrane is fully charged, demonstrating an induced permeability of the membrane to hydrophilic molecules. This phenomenon is most fully explained by models involving the formation of transient pores in the membrane due to exposure to the external EF. Two critical parameters influence the reversibility of this electropermeabilisation: the magnitude of the induced transmembrane potential, and the duration of the exposure to the external EF. For cells, transmembrane potentials above 1 V and longer pulse times lead to irreversible permeabilisation and cell death. The transmembrane potential induced by an external EF depends upon the radius of the cell membrane, with larger cells suffering a greater transmembrane potential from a given EF. Hence, the magnitude of the field needed to inactivate yeast cells is generally lower than that needed to inactivate bacteria [48]. Death occurs due to either (i) the formation of permanent pores and subsequent destabilisation of the cell membrane or (ii) loss of important cell components and destruction of chemical gradients via transport through transient pores [50]. If electrochemically generated oxidants are present, these pores may allow the oxidants free access to the interior of the cell, aiding the inactivation process [49].

A great deal of research has focused upon the use of EFs and current to kill bacteria and yeast in industrial and medical applications, as illustrated by the following examples. Drinking water contaminated with *E. coli* K12 (100 cells cm^{-3}) was disinfected at a rate of 600 cells cm^{-3} h^{-1} with the application of a 0.7 V electric potential using a carbon cloth electrode [51]. Drinking water contaminated with 335 cells cm^{-3} total coliforms and 1035 cells cm^{-3} fecal streptococci was sterilised with a

2.5 mA cm^{-2} direct current density (125 mA current) applied with 5 cm × 5 cm titanium electrodes for 30 min [52]. Direct current (60 mA) was used to inhibit the growth of *E. coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* contaminants of a bioprocess reactor [49,53].

Few such studies have been conducted with viruses, however. One would expect viruses to be more resistant to electrochemical inactivation than bacteria. For example, some viruses (notably bacteriophage) are not enveloped with a membrane and would be immune to inactivation processes involving irreversible membrane permeabilisation. Even enveloped viruses would be more resistant than their cellular counterparts due to their smaller size. Viruses also tend to be more resistant to chemical disinfectants, such as chlorine and ozone, than vegetative bacteria [49]. Recently, bacteriophage MS2 was suggested as a model for the study of the biological effects of EFs, mainly due to its relatively simple biology compared to prokaryotic and eukaryotic cells [49]. When exposed to an induced 60 Hz EF, a lag in MS2 yield was demonstrated, but the overall phage yield was totally unaffected [49]. Should viruses prove more resistant to electrochemical inactivation than bacteria as these results suggest, technologies using electric current to kill bacteria [54] may not be sufficient to ensure treated food or drinking water is safe from viruses [49].

4. Electrochemical technologies in wastewater treatment

Using electricity to treat water was first proposed in UK in 1889 [55]. The application of electrolysis in mineral beneficiation was patented by Elmore in 1904 [55]. Electrocoagulation (EC) with Al and Fe electrodes was patented in the US in 1909. The EC of drinking water was first applied on a large scale in the US in 1946 [55]. Because of the relatively large capital investment and the expensive electricity supply, electrochemical water or wastewater technologies [56] did not find wide application worldwide then. Extensive research, however, in the US and the former USSR during the following half century has accumulated abundant amount of knowledge. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, ET have regained their importance worldwide during the past two decades [57]. There are companies supplying facilities for metal recoveries, for treating drinking water or process water, treating various wastewaters resulting from tannery, electroplating, dairy, textile processing, oil and oil-in-water emulsion, etc. Nowadays, ET has reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact [58]. For some situations, ET may be the indispensable step in treating wastewaters containing refractory pollutants [59,60]. Chen [55] has examined the established technologies such as EC, electroflotation and electrooxidation (EO) for metal recovery. For books dealing with environmentally related electrochemistry, the readers are referred to other publications [12] and those cited by Chen [55].

5. Electrodisinfection technologies

In ED, electrodes (at least one cathode and one anode) are inserted either directly into the volume of water to be disinfected, or into a bypass pipe. A DC voltage is applied between the electrodes, leading to the electrolysis of the water. At the anode the main product is oxygen (Eq. (1)):

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

accompanied by an acidification of the water in the vicinity of the anode. At the cathode, hydrogen is formed (Eq. (2)):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

and the water near the cathode becomes alkaline. Since the evolved hydrogen is generally unwanted, it must be separated from the water stream. Because only small amounts are formed at normal currents (about 0.4 litres of hydrogen is produced per amp-hour (Ampere × hour =3600 Coloumb)), this is possible without problems in most cases [15].

In most practical applications, simple undivided electrochemical reactors employing parallel-plate, monopolar electrode stacks are inserted into the reactor pipe. The electrode plates may be configured as unperforated or perforated plates, or as expanded metal. Recently, an ED process which completely avoids hydrogen production has been developed. Atmospheric oxygen is reduced to hydroxyl ions at a gas diffusion cathode [15] (Eq. (3)):

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (3)$$

Here the cathodic reaction (Eq. (3)) replaces the hydrogen producing reaction (Eq. (2)). The gas diffusion electrodes are composed of a porous graphite-polytetrafluoroethylene (PTFE) layer, in contact with a metal mesh as current collector, and backed by an oxygen-permeable PTFE layer to prevent water leakage. The graphite carries a manganese oxide catalyst which eliminates unwanted hydrogen peroxide [15].

5.1. Production of free chlorine from the chloride content of the water

If ED is applied to drinking water, industrial water, seawater or other solute-containing water, its effect is mainly based on the electrochemical production of hypochlorite and/or hypochlorous acid from the chloride content of the water. The effectiveness of this method has always been accepted for water which contains higher concentrations of chloride ions, such as seawater with about 19 g L^{-1} chloride, or where large amounts of sodium chloride have been added, for instance to swimming pool water (chloride concentrations here are usually about 2–5 g L^{-1}). For the disinfection of drinking water and other waters with much lower chloride content, the effectiveness of the method was not clear for a long time [52]. It was eventually demonstrated that even at very low chloride concentrations (less than 100 mg L^{-1}) sufficient free chlorine can be produced to efficiently disinfect water [15].

The disinfectant hypochlorous acid/hypochlorite is produced at the anode in a side reaction to oxygen evolution. The following simplified reaction mechanism is proposed. First, chlorine is produced electrochemically from chloride ions dissolved in the water (Eq. (4)):

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{4}$$

Chlorine hydrolyses in water and hypochlorous acid (HClO) is formed [15] (Eq. (5)):

$$Cl_2 + H_2O \rightarrow HClO + HCl \tag{5}$$

Hypochlorous acid and the hypochlorite anion form a pH-dependent equilibrium [15] (Eq. (6)):

$$HClO \leftrightarrow ClO^- + H^+ \tag{6}$$

In the nomenclature of water disinfection, the sum of hypochlorous acid and hypochlorite concentrations is usually termed 'free chlorine' or 'active chlorine'. The disinfecting effect of free chlorine is based on the release of atomic oxygen according to Eqs. (7) and (8) [15]:

$$HClO \rightarrow O + Cl^- + H^+ \tag{7}$$

$$ClO^- \rightarrow O + Cl^- \tag{8}$$

During the disinfection, chloride ions which have been consumed by electrochemical free chlorine production are reformed. Thus there is no overall change in the chemical composition of the water during electrochemical water disinfection. Where there is a low chloride concentration in the water to be treated (as in drinking water) the current efficiency of the electrode material for the production of free chlorine is crucial; it should be as high as possible. Great differences have been found in the efficiency of free chlorine production between different electrode materials [61] at low chloride concentrations [15].

5.2. Ozone production

If water with low or zero chloride concentration is required, the addition of sodium chloride is not acceptable and free chlorine cannot be produced in situ. Disinfection must therefore be based on other electrogenerated species. By using anodes with a high oxygen overvoltage, a high current density and a low water temperature it is possible to produce ozone directly from the water according to Eq. (9):

$$3H_2O \rightarrow O_3 + 6e^- + 6H^+ \tag{9}$$

Electrochemical ozone production has been known since the nineteenth century [15]. Electrolysis was the first production method for ozone, but for most applications ozone is now produced by corona discharge. The disadvantages of electrolytic production include too low a current efficiency, complicated production systems, unstable electrode materials (such as lead oxide (PbO_2) anodes) and/or difficult-to-handle electrolytes. Electrolytic production may become more attractive using a new simple electrode assembly of a 'sandwich' configuration: diamond anode/SPE/cathode sandwich [15].

5.3. Disinfection or germ minimisation by electrochemically produced oxygen

In some applications, electrolytically produced oxygen, the main anodic reaction product, shows some germicidal activity. This is especially true if anaerobic bacteria are the disinfection target. An example of this type of application is the wash water cycle of car wash stations. Here, the formation of anaerobic digestion products often leads to bad odours. Anaerobic conditions are eliminated *via* the fine dispersion of bubbles of electrolytically produced oxygen in the water. This is a highly effective mode of dissolution. For this application, Pt-coated electrodes are the most suitable anodes, because the main germicidal effect is based on electrolytically produced oxygen and not on free chlorine [15].

5.4. Disinfection by cathodically produced hydrogen peroxide

While most of the possible disinfectants in electrochemical water treatment are produced at the anode, hydrogen peroxide may also be produced at the cathode. This process has been used [15] for water disinfection (Eq. (10)):

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \tag{10}$$

Oxygen dissolved in the water may serve as the reactant in Eq. (10). The maximum concentration of oxygen in water which is in equilibrium with air at 25ºC is about 10 mg L^{-1} (0.3 mmol L^{-1}). The oxygen produced by the anodic half reaction according to Eq. (1) can also be used for the cathodic production of hydrogen peroxide. In this case, higher concentrations of dissolved oxygen are possible, because the water is in contact with pure oxygen, and not merely with air. It is also possible to use a gas diffusion cathode on which the oxygen from the surrounding air is reduced to H_2O_2. In terms of energy efficiency, the electrode material best suited to H_2O_2 production is graphite. This material (without additional catalysts) is also the core component in gas diffusion electrodes for H_2O_2 production. Because of its lower oxidation potential, H_2O_2 is a less effective disinfectant than free chlorine or ozone. Therefore, higher concentrations and/or longer disinfection times are necessary, limiting its applicability. Hydrogen peroxide has the advantage that its disinfectant action produces neither by-products nor residues [15].

5.5. Inactivation of microbes by electro-oxidation

Inactivation of microbes by EO may happen in two different ways [55]. The first is the direct anodic oxidation. Bacteria cells are destroyed at the electrodes surface by hydroxyl radicals generated from water by electrolysis (Eq. (11)) [55,62–64]. Hydroxyl radical is the most powerful oxidant and it can cause oxidative stress against cell of bacteria. The second way is indirect electrochemical oxidation when microbes are destroyed by electrochemically generated ozone (Eqs. (12–14)) [55,62] or hydrogen peroxide (Eq. (15)) [42]. Many papers have also investigated the inactivation mechanism by chlorine and/or hypochlorite (Eqs. (4–6)) [56]:

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e^- \tag{11}$$

$$^{\bullet}OH \rightarrow {}^{\bullet}O + H^+ + e^- \tag{12}$$

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \tag{13}$$

$$^{\bullet}O + O_2 \rightarrow O_3 \tag{14}$$

$$2^{\bullet}OH \rightarrow H_2O_2 \tag{15}$$

The anode material has a very important role in EO reactions. It should be stable even in extreme conditions (low pH, high current density) and have sufficient catalytic activity to form oxidants either directly on its surface (hydroxyl radicals) or indirectly (chlorine, ozone). Anode materials investigated include for example PbO_2 [65] the so-called DSA [66] and diamond films. Recently, boron-doped diamond (BDD) electrode has especially given good results [42,67] because it has the highest oxygen evolution overpotential of all known electrode materials. It means that higher amount of used DC current is spent to form oxidants instead of in the oxygen evolution reaction (Eq. (13)) which is useless reaction for inactivation of microorganisms [56].

6. Disinfection by chlorination, ozonation and the fenton reaction

The electrochemical method was highly effective for wastewater disinfection. An *E. coli* killing efficiency of 100% could be achieved for the model water with a contact time of only 0.5 min and a current density of 25 mA cm^{-2}. When the current density was reduced to 16 mA cm^{-2}, a contact time of 2 min was needed to provide a disinfection efficiency of 99.98%. ED was much more effective than conventional chlorination [68]. A contact time of at least 30 min was required for chlorination to have a bactericidal efficiency of 99.94% or higher. ED appeared to have a germicidal effectiveness even greater than ozonation in terms of treatment time. The Fenton reaction was not shown as the most powerful disinfection means for the model water; however, this was likely caused by the low dosage of Fenton's reagent employed in the experimental tests compared to most Fenton reaction conditions [69].

In general, all of the disinfection methods examined here, ED, chlorination, ozonation and the Fenton reaction, were effective in killing *E. coli* with an initial density of 10^8 mL^{-1} in the model wastewater. With a killing efficiency of 99.4% or higher, almost all of the cells in the treated samples lost their viability from the viewpoint of being biologically available to incubation. Nonetheless, regardless of viability, all of the cells and related cellular materials in a sample would be retained on the filters for scanning electron microscopy (SEM) observation [69].

6.1. Scanning electron microscopy examination of disinfected E. coli cells

Fresh *E. coli* cells receiving no disinfection were full with smooth surface appearance. For the samples after chlorination, the cell surface became slightly rough. However, there were no severe surface defeats and cell lysis shown for these cells. It is generally agreed that a low dosage of chlorine does not cause cell destruction [70]. During chlorination, chlorine diffuses through the cell walls, produces a dysfunction in the internal enzyme groups and hence inactivates cells [70]. It also has been reported that chlorine may react with the cell wall materials. For example, chlorine could oxidise the N-terminal amino groups of proteins within the cell wall, which would alter the wall strength and thus kill the cells. In general, nonetheless, the action of chlorine does not affect the integrity of cells, as shown by the SEM micrograph [69].

More changes in the sample morphology were observed for the cells after ozonation. In addition to cell surface roughness, there were also a few 'spots' on the cell surface and impurity precipitates on the filter, which could be cellular constituents leaked from the cells during ozonation. Ozone used in water and wastewater treatment can be classified as both an oxidant and a germicidal compound. Its potent disinfection property has been attributed to its high oxidation potential. It has been indicated that ozone disinfection is a direct result of cell wall disintegration and cell lysis [70]. Previous SEM examination on ozonated algal cells revealed drastic damage of the cell surface architecture. In the presence of ozone, the macromolecules released from the cells could be further cleaved and oxidised, resulting in much smaller molecules. Although the present SEM analysis showed evidences of cell lysis after ozonation, major accumulation of cellular materials was not observed on the filter. It is likely that the high ozone dosage, 10 mg L^{-1}, applied in the test had oxidised the organic materials of cell lysis or convert them to small molecules that would not be collected on the membrane filters [69].

E. coli cells treated by the hydroxyl radical produced by the Fenton reaction showed a great deal of release of cellular constituents. Deformation of cell surface also can be observed. Reactive oxygen species (ROS), such as free radicals of $^{\bullet}OH^{-}$ and $O_2^{\bullet -}$, are thought to cause damage to the cell membrane [71]. The loss of membrane permeability would lead to swelling and rupture of the cells. The present SEM observation for the samples treated by the Fenton reaction confirmed that $^{\bullet}OH^{-}$ radicals could lead to severe surface damage and rupture to the cells, resulting in massive cell lysis [69].

In cell samples after ED, slight surface deformation was observed. More importantly, a large amount of cellular materials were released from the disinfected cells, which were collected and shown on the SEM filters. These SEM images were rather close to that treated by the Fenton reaction. The similarity in sample appearance shared by ED and the radical reaction suggested that during ED, *E. coli* was most likely damaged by the chemicals with properties similar to $^{\bullet}OH^{-}$ radicals rather than chlorine. As previously hypothesised [52,72], the ED process could produce intermediate chemical species as free radicals which have oxidising potentials higher than that of chlorine or even ozone. These strong oxidants could attack the cell membrane and wall, bringing in massive cell kills and lysis, as illustrated by the SEM micrographs [69].

6.2. *Role of free radicals in the germicidal actions of electrodisinfection*

The Diao et al.'s study [69] further demonstrated the superior effectiveness of ED. SEM examination of disinfected *E. coli* cells also provided valuable indication for the underlying killing action of ED in relation to other disinfection means. The results are particularly in favour of the hypothesis about the germicidal role of free radicals generated during the ED process [69].

Electro-chlorination (E-C) has been considered as a principal function of ED [52,73,74]. There are also other hypotheses that attribute bacterium killing to the destruction and inactivation of cells in the EF formed during the ED treatment [72,75–77]. However, such hypotheses have been largely undetermined by the Li et al. [72]'s experimental findings [72]. A comparison between the saline and freshwater sewage effluents showed that ED was not nearly as effective for the freshwater sewage as for the saline effluent, although more favourable conditions to killing by EF, such as higher current densities, were provided for the freshwater sewage effluent [72]. Therefore, inactivation by the EF could not be regarded as a prevailing killing function of the ED process [69].

Chloride ions appeared to play a critical role in ED. Chlorine formation by electrolysis certainly contributed to ED inactivation [78]. However, E-C may not be sufficient to reconcile the germicidal effectiveness observed for ED. Other killing mechanisms may be more important than E-C during ED treatment. Based on the SEM examination, samples after chlorination and EDs were different in cell morphology and surface structure. No significant lysis was found for the chlorinated cells, while severe lysis was observed for the ED treated cells [69].

As suggested above, the high capacity of ED may be provided by short-lived and energy rich intermediate products with a more powerful germicidal capability. These chemical products apparently include free radicals, such as $^{\bullet}OH^{-}$ and $O_2^{\bullet -}$ [72,79,80]. The present SEM study provides more proof of the theory about the major role of $^{\bullet}OH^{-}$ radicals in ED. Cell samples treated by $^{\bullet}OH^{-}$ radicals of the Fenton reaction had a rather similar appearance as those after ED. There was substantial disintegration and lysis of the cells resulting from both the Fenton reaction and ED treatment. Released cellular materials were accumulated on the filters, which was noticeable to a lesser extent for the samples of ozonation and hardly noticeable for the samples of chlorination. Therefore, in addition to E-C, *E. coli* cells during ED were likely inactivated by the intermediate products with an oxidising power similar to that of free radicals and much stronger than that of chlorine [69].

A new hypothesis about the role of chloride ions in the disinfective action of free radicals is also worth noting for further elucidating the mechanism of ED. The new theory suggests that chloride ions in solution are a catalyst for the chain reactions of a cyclic process that involves $^{\bullet}OH^{-}$ radicals [81]. With excess Cl^{-}, the chain reactions are driven in the direction to extend the lifetime of $^{\bullet}OH^{-}$ by a factor of 10 or so, which makes the radicals many times more effective to cell destruction. Therefore, it can be speculated that Cl^{-} also acts as a catalyst in a germicidal function embracing free radicals, rather than only as a precursor of Cl_2 formation, in ED [69].

7. From chemical disinfection to electrodisinfection

7.1. Chemical disinfection and electrodisinfection

Chlorine has been widely used in water disinfection to eliminate of waterborne diseases. However, an important drawback is the formation of harmful chlorination disinfection by-products (CDBPs) [82]. Since the pioneering work of Rook [83], more than 700 CDBPs had been reported [84]. Many investigations have been conducted in the precursors and the formation of CDBPs. In a broad spectrum of compounds, NOM is generally regarded as the main precursor of CDBPs in source water [85]. Meanwhile, except NOM, there exist large quantities of toxic organic compounds (TOC) in source water, especially in micro-polluted source water. Though the concentrations of them are generally in the level of ng L^{-1} to µg L^{-1}, the contribution of TOCs to CDBPs is significant due to their high activities with chlorine. To control DBPs in drinking water [86], some water treatment technologies, e.g., enhanced coagulation, nanofiltration and reverse osmosis, are employed to remove DBPs precursors before disinfection [87,88]. Because of their high water solubility and low molecular mass, some of these TOCs are difficult to be reduced in contrast to NOM in water treatment. Thus, more efforts should be performed to investigate the formation characteristics and influential factors of CDBPs from TOC in water disinfection [18,89].

There are three reasons why ED has arrived at technical maturity only recently, rather than earlier in the (possibly) 2000 years since its discovery:

(a) Sufficiently stable and efficient electrode materials for ED have been developed and optimised only in the last forty years. These are titanium electrodes with mixed oxide coatings based on iridium and/or ruthenium oxide, and amond electrodes [15].
(b) The functional interrelationships between chloride concentration in the water, current, current density, electrode material, water quality, electrochemical production of free chlorine and disinfecting action have been investigated in detail only recently [15].
(c) Development work on ED has often been undertaken by amateurs in both electrochemistry and water chemistry, and this remains somewhat true today. Only a few electrochemists have been interested in this topic, mostly only for a short period in their career. This has resulted in mistakes in device dimensioning and in unscientific explanations of the mechanism of the process [15].

Conventional disinfection methods may be divided between chemical and physical processes. In chemical processes, disinfecting substances such as ozone, chlorine, sodium hypochlorite or chlorine dioxide are added to the water to be treated. These processes are reliable, and have proven their efficiency over many decades. They not only kill microorganisms, but also provide a disinfection reservoir which protects the water against recontamination for a certain time. A frequent drawback of the chemical processes is unwanted side reactions of the disinfectants with substances present in the water. These reactions lead to DBPs, some of which are considered dangerous. There are also hazards in producing, transporting and handling large amounts of such substances as chlorine and ozone [15].

In physical disinfection processes the microorganisms are removed or killed by means of irradiation with ultraviolet or ionising radiation, heating to elevated temperatures, ultrasound, or separation through membrane filtration. The main drawback of the physical disinfection methods is the lack of a reservoir effect. These processes are only effective in the immediate surroundings of their operating devices [15].

As compared with other chemical disinfection methods, the advantages of ED are obvious: no transport, storage and dosage of disinfectants are required. The disinfecting effect can be adjusted according to the on-site demand. ED shows a reservoir effect and is often more cost-effective and requires less maintenance than other disinfection methods. Photovoltaic power supply makes it possible to use ED far from the electrical supply grid. This may be important for its application to drinking water in developing countries. ED can also be used in conjunction with other disinfection methods [15].

7.2. Electrodisinfection: direct electrolysers vs. mixed oxidant generators

Drinking water disinfection has been a major contributor to the reduction in world mortality and morbidity figures during the last century [90]. It has been responsible for almost eliminating life-threatening disease such as cholera and typhoid in the USA [91]. Despite this, at the turn of the 21st century 1.2 billion people still did not have access to safe drinking water [91]. Drinking water disinfection occurs throughout the multibarrier water treatment processes of settlement, coagulation, and filtration or through chemical treatment processes, such as chlorination or ozonation. The disinfection process can be considered to have two purposes, primary disinfection, the removal or inactivation of microbiological contaminants in the raw water supply, and the provision of a residual in the distribution network. Chlorine is the most commonly used chemical method of disinfection providing both primary and residual disinfection [91].

Despite chlorine's effectiveness as a method of drinking water disinfection, it has several disadvantages, which are the cause of consumer and regulatory pressure on water supply companies. These disadvantages cause consumer and regulatory pressure on water supply companies and include unfavourable taste and odour associated with the use of chlorine in drinking water, ineffectiveness when used alone against resistant microorganisms such as *Cryptosporidium parvum*, occasional regulatory failures, and the generation of potentially toxic DBPs [91].

As a result of these disadvantages a number of alternatives to chlorine for drinking water disinfection have been suggested. The alternatives are wide ranging including chemical systems, such as ozone, silver, copper, ferrate, iodine, bromine, hydrogen peroxide and potassium permanganate; physiochemical systems, such as titanium photocatalysis, photodynamic disinfection and ED, and physical systems, such as ultraviolet irradiation, ultrasonication, pulsed EFs, irradiation, magnetic enhanced disinfection and microwave systems. ED has emerged as one of the most promising of the alternatives to chlorine providing both primary and residual disinfection. The potential use of electrochemical systems for disinfection has been discussed since the 1950's, but systems other than those generating chlorine, have yet to gain widespread acceptance within the water industry [16].

On the other hand, ED devices can be separated into two categories, direct electrolysers and mixed oxidant generators. Direct electrolysers interface directly with contaminated water, whilst mixed oxidant generators use a concentrated brine solution to generate "anolyte" which is a mixture of strong oxidising species including free chlorine, chlorine dioxide, hydrogen peroxide, ozone, and other short-lived radicals [91].

Numerous cell configurations and electrode materials have been investigated for ED against a variety of microorganisms. The effectiveness of the electrochemical cells to disinfect bacteria, viruses, and protozoa has been shown to vary. Mixed oxidant generators have been reported to successfully inactivate *Clostridium perfringens* (>2.3 log), Coliphage MS2 (>2.5 log), *E. coli* (>2.5 log), and *Cryptosporidium parvum* oocysts (2.6 log), whilst direct electrochemical treatment has been shown to be possible against a variety of bacteria [39,51,52,91].

The inactivation efficacy of ED systems is largely dependent on cell configuration, electrode material, electrolyte composition, the microorganism and other experimental parameters, such as flow rate and current density [39,51,52]. The presence of chloride in the electroyte will increase the cells inactivation efficacy generating highly germicidal active chlorine species [69], whilst $H_2PO_4^{2-}$, HCO_3^-, and CO_3^{2-} have an inhibitory effect on the inactivation efficacy of electrochemical reactors [91]. It is postulated that electrochemical systems, which generate excess amounts of chlorine species will have the same major disadvantages for drinking water disinfection as chlorine. However, the debate as to whether electrochemical systems can replace chlorine is still open. Conflicting research concerning the generation of DBPs (THMs) in natural water treated with electrochemically generated mixed oxidants has reported more than 50% reduction in total THMs [91]. However, Kerwick et al. [91] concluded that ED can be effective without the generation of chlorine species.

Other advantages of ED also need to be considered including the benefits of onsite generation, and the avoidance of handling and storing hazards associated with chlorine gas and hypochlorite [91].

7.3. Virus removal: coagulation vs. electrocoagulation

EC has been widely studied in water and wastewater treatment [92] to remove heavy metals, organics, bacteria, hardness, turbidity, and other contaminants [93–97]. In the EC process, the electrodes are consumed as the coagulant is generated and precipitated; no liquid chemical is added; alkalinity is not consumed; and pH adjustment is not needed. Additionally, compared with chemical coagulation (CC) [98], the EC process reportedly requires less coagulant and produces less sludge [93,96]. According to one estimate, the space required for EC is less than CC because EC does not require chemical storage, dilution, and rapid mixing [96]. Because EC systems typically use solid Fe or Al anodes rather than corrosive Fe or Al salt solutions, EC units can be more easily incorporated into "packaged" plants and transportable water treatment plants for use in remote areas or in emergency water supply treatment [99].

Zhu et al. [99] concluded that EC significantly outperformed CC for virus removal. The proposed mechanism for this improved performance by EC is that locally higher Fe and virus concentrations and locally lower pH near the anode improved viruses enmeshment by Fe flocs as well as adsorption of viruses onto the Fe floc particles [99].

Roa-Morales et al. [100] evaluated the removal of organic pollutants from pasta and cookie processing industrial wastewater by Al EC and combined EC/H_2O_2 processes using a pilot batch reactor. Under optimal conditions of pH 4 and 18.2 mA m^{-2} current density, the electrochemical method yields very effective removal of organic pollution. Treatment reduced chemical oxygen demand (COD) by 90%, biochemical oxygen demand (BOD_5) by 96%, total solids by 95% and fecal coliforms by 99.9%. The effect of reducing the pH of the aqueous solution with sulfuric acid on the chemical species formed and its effect on the sludge phase formation was determined. The wastewater quality was monitored using UV–vis spectrometry and cyclic voltammetry in order to characterise raw and treated wastewater. Finally, the morphology and elemental composition of the resulting sludge was characterised using SEM and energy dispersion spectra (EDS).

On the other hand, the EC process involves the generation of coagulants in situ by electrolytic oxidation of the sacrificial electrode materials. The materials employed in EC are usually Al or Fe. The electrodes can be made of Al or Fe plates or from scraps such as Fe or Al millings, cuttings, etc. Because there are a definite amount of metal ions required to remove a given amount of pollutants, it is usual to use Fe (Fig. 2 (a) and (b)) for wastewater treatment and Al (Fig. 2 (c)) for water treatment. The Al plates are also finding applications in wastewater treatment either alone or in combination with Fe plates due to the high coagulation efficiency of Al^{3+} [55]. Mollah et al. [101] have reported that the electrolytic dissolution of the Al anode produces the cationic monomeric species such as Al^{3+} and $Al(OH)_2^+$ at acidic conditions (Fig. 2 (c)). At appropriate pH values, they are transformed initially into $Al(OH)_3$ and finally polymerised to $Al_n(OH)_{3n}$ according [101] to the following reactions [102]:

$$Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^- \tag{16}$$

$$Al_{(aq)}^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H_{(aq)}^+ \tag{17}$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \tag{18}$$

However, depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ may also be present in the system. In addition, various forms of charged multimeric hydroxo Al^{3+} species may be formed under appropriate conditions. These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption. The authors have also reported that Fe upon oxidation in an electrolytic system produces iron hydroxide, $Fe(OH)_n$, where n =2 or 3. Two mechanisms have been proposed for the production of $Fe(OH)_n$ [101]. The first mechanism (Fig. 2 (b)) for the production of $Fe(OH)_3$ consists of Eqs. (19) and (20) for anode, Eq. (21) for cathode, and Eq. (22) for the overall reaction as follows [102]:

$$4Fe_{(s)} \rightarrow 4Fe_{(aq)}^{2+} + 8e^- \tag{19}$$

$$4Fe_{(aq)}^{2+} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H_{(aq)}^+ \tag{20}$$

$$8H_{(aq)}^+ + 8e^- \rightarrow 4H_{2(g)} \tag{21}$$

$$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \tag{22}$$

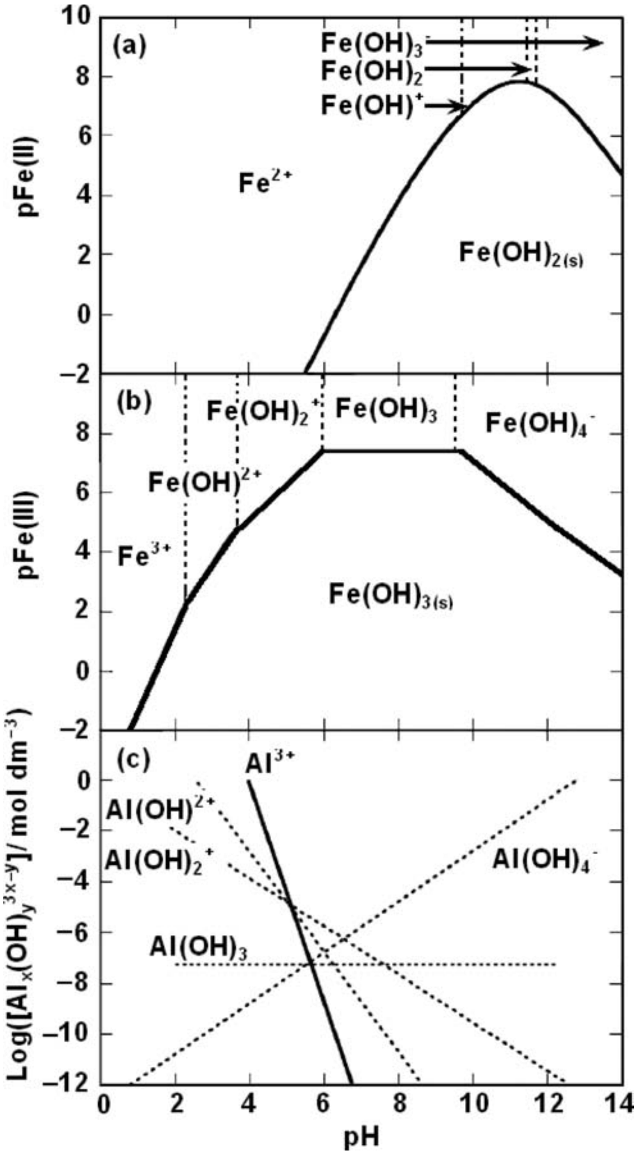

Fig. 2. Predominance-zone diagrams for (a) Fe(II), (b) Fe(III), and (c) Al(III) chemical species in aqueous solution. The straight lines represent the solubility equilibrium for insoluble $Fe(OH)_2$ and $Fe(OH)_3$, respectively, and the dotted lines represent the predominance limits between soluble chemical species [92].

The second mechanism (Fig. 2 (a)) for the production of $Fe(OH)_2$ consists of Eqs. (23) and (24) for anode, Eq. (25) for cathode, and Eq. (26) for the overall reaction as follows [102]:

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2e^- \tag{23}$$

$$Fe_{(aq)}^{2+} + 2OH_{(aq)}^- \rightarrow Fe(OH)_{2(s)} \tag{24}$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^- \tag{25}$$

$$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \tag{26}$$

The $Fe(OH)_{n(s)}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation. In addition, the H_2 produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation [101,102].

7.4. On-line production of ferrate with an electrochemical method and its potential application for wastewater treatment

Ferrate(VI) salts (e.g., potassium ferrate) are very strong oxidants [103]; under acidic conditions, the redox potential of ferrate(VI) ions is the strongest (Table 1) among all oxidants/disinfectants (E^0 =+2.20 V) used for water and wastewater treatment [104]. It is also a coagulant; during the oxidation/disinfection process, where ferrate(VI) ions (oxo-anions of Fe(V) and Fe(VI)) [105] are reduced to Fe(III) ions or ferric hydroxide, which simultaneously generates a coagulant in a single dosing and mixing unit process [106].

A number of studies on the oxidation of various organic/inorganic contaminants by ferrate(VI) were reported in 1980s and 1990s, which have been reviewed by several authors [45,103,107–109]. The superior performance of ferrate(VI) as an oxidant/disinfectant and coagulant was demonstrated by several researchers [110,111]. Therefore, it is important to explore the application of ferrate(VI) for water and wastewater treatment practice [112], and for environmental remediation [106].

However, challenges have existed to the implementation of ferrate(VI) technology in water and wastewater treatment practice [113]. Fe(VI) solutions are generally unstable; their decomposition by reduction to Fe(III) species occurs rapidly at room temperature. The instability may be retarded but not stopped at low temperatures or with careful control of solution concentrations. Hence, without steps of refrigeration or high purification, the solutions cannot be stored for use in practice. Solid ferrate(VI) salts are stable, but they are costly as they require multiple chemical reagents and long synthesis time. This makes it difficult to be used in industry. In order to solve the problems of instability and the high cost of using ferrate(VI), it would be an ideal approach to generate ferrate in situ and apply the generated ferrate(VI) directly for wastewater treatment [106].

The ferrate can be synthesised by the chemical, thermal, or electrochemical methods [113]. The main advantage of the electrochemical synthesis in comparison to the other two methods is the high purity of the product, and the utilisation of an electron as a so-called "clean oxidant" [114]. In addition, this approach results in a substantial reduction of the amount of solvents needed to produce ferrate of high purity [115]. The synthesis of ferrate by an anodic iron dissolution proceeds in the transpassive potential region. At these conditions the surface of the iron anode is covered by a partly disintegrated (e.g., containing cracks and/or pores) oxidic layer. The synthesis efficiency is strongly influenced by the protective properties of this layer. These properties can be influenced by the reaction conditions, i.e., by the electrolyte concentration, composition and temperature, cell arrangement, and by the anode material composition [116]. A good review on electrochemical synthesis of ferrate(VI) may be found elsewhere [117].

8. Potable water treatment by electrocoagulation

Coagulation using chemical coagulants is one of the most essential processes in the conventional treatment of drinking water. However CC has some inherent problems in cost, maintenance, and sludge production. Thus EC has recently been suggested as an alternative to conventional coagulation. Several reports [96,118–125] have

Table 1
Redox potential for the oxidants/disinfectants used in water and wastewater treatment [103].

Disinfectant/oxidant	Reaction	*E*° (V)
Chlorine	$Cl_2 + 2e^- \leftrightarrow 2Cl^-$	1.358
	$ClO^- + H_2O + 2e^- \leftrightarrow Cl^- + 2OH^-$	0.841
Hypochlorite	$HClO + H^+ + 2e^- \leftrightarrow Cl^- + H_2O$	1.482
Chlorine dioxide	$ClO_{2(aq)} + e^- \leftrightarrow ClO_2^-$	0.954
Perchlorate	$ClO_4^- + 8H^+ + 8e^- \leftrightarrow Cl^- + 4H_2O$	1.389
Ozone	$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + H_2O$	2.076
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.776
Dissolved oxygen	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	1.229
Permanganate	$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2 + 2H_2O$	1.679
	$MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$	1.507
Ferrate(VI)	$FeO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Fe^{3+} + 4H_2O$	2.20

been published in scientific journals on EC combined with electroflotation for treating potable water [126].

An EC process for potable water treatment was studied by Vik et al. [119]. Some laboratory experiments including a DC power supply (6–12 V), resistance box to regulate current intensity, and a multi-meter to read the values were performed. In the electrochemical cell four plate aluminium anodes and cathodes (dimension $14 \times 20 \times 0.25$ cm) were used as electrodes, at a flow rate of 0.171 L min^{-1}. This process was compared with a conventional water treatment process and was an effective process for use in small water treatment plants because of the following:

- The amount of chemicals having to be transported to the solution is lower than for chemical treatment (approx. 1/10 of the amount).
- The maintenance and operation of the EC system will be simple.
- A lesser amount of sludge is formed in an EC system [126].

The research studies showed that EC process [127,128] is more efficient than coagulation process for potable water treatment. Less aluminium dosage was needed to get the same removal efficiency in EC process, which is related to chemical cost and sludge production [126].

9. Electrodisinfection by-product: chlorine dioxide

Chlorine dioxide is a poisonous gas that can be explosive at partial pressures higher than 300 mmHg. Unfortunately, it is not stable over a long time and must be prepared in situ. Reports about a longer storage mostly relate to chemical solutions for chlorine dioxide preparation. Nevertheless, stock solutions can be stored in the cold over many days with relatively small losses of chlorine dioxide. Chlorine dioxide decomposes under UV light; it reacts with impurities, mainly to chlorite and to chlorate. In a more or less slow reaction, it may react with active chlorine components (dissolved chlorine, hypochlorous acid, hypochlorous ions) depending on pH and concentration levels, forming a non-stable intermediate Cl_2O_2 [129]. Problems with respect to the formation of chlorite which is a hazardous component limited by law [130] in drinking water have been discussed recently [129]. Chlorine dioxide as a disinfectant may form DBPs, but in a much lower extent than chlorine. It is assumed that THM formation and reactions with ammonium are not possible [131]. Chlorine dioxide is a highly efficient disinfectant [132] and widely used in water disinfection and treatment technologies for removal of bad odours or biofilms in pipe systems (*Legionella* problem) [129].

9.1. Possibilities and problems of the electrochemical ClO_2 production

Two lines of chemical chlorine dioxide production are known based on reactions of chlorate or chlorite with concentrated acids, such as HCl, H_2SO_4 or with peroxidisulphates. Using electrolysis, three production lines are known starting with the anodic or cathodic treatment of chlorite and chlorate solutions correspondingly, mostly in divided cells and known for example under the name of *Olin Technologies* [129]. A third electrochemical method is the electrolysis of chloride containing waters. Little is known about the kinetics of chemical and especially electrochemical reactions. Most of work has been carried out by the Gordon group [129] analysing chlorine chemistry and problems of by-product analysis (so-called mixed oxidants) mainly for chlorination, or in liquors of chlorine disinfectants produced electrochemically. The studies resulted in many interesting data but its application for the disinfection electrolysis of water is not possible without limitations. Basically, peculiarities as mentioned below make the direct electrochemical water treatment still more complicated [129]:

- Electrochemical reactions generate components, which further can take part in equilibrium, consecutive or parallel reactions of electrochemical and chemical nature. Applying a simplified consideration, at least three reaction zones with different conditions exist for these reactions. The first zone is the contact plane and vicinity of the anode with acidic pH due to the main reaction of oxygen formation (Eq. (1)). Because the current efficiency in the chloride concentration range for drinking water until 250 mg L^{-1} is mostly about some percent as calculations show, reaction (1) or the production of oxygen ions is dominating. The second zone is the contact plane and vicinity of the cathode with enlarged basic pH due to the main reaction of hydrogen formation (Eq. (2)). Finally, as a third zone, the bulk of electrolyte can be considered. pH Values between 6.5 and 9.5 are usually allowed here in congruence with drinking water regulations. The water electrolysis is not balanced, chlorine components undergo several reactions, and changes in pH, mostly to higher pH, occur during electrolysis in non-divided cells [129].
- Oxidants generated at the anode may be reduced at the cathode in a non-divided cell. Larger current densities can both increase and decrease the efficiency of those side reactions due to higher migration and diffusion rates [129].
- In the course of electrochemical processes, products and product combinations, which are not allowed, may be formed. For example, chlorine dioxide, chlorite, chlorate, nitrite and ozone have been identified [129].

- The large variety of water electrolyte composition, different technologies and the variation of electrochemical parameters, such as temperature, concentration relations, polarisation and electrode material result in a much larger complexity of reactions, which cannot be overseen until now. Obtained reaction matrices show usually a totally other behaviour to chemicals addition as compared for electrochemically prepared disinfection liquors [129].

Bergmann and Koparal [129] concluded that:

1. Higher current densities support higher chlorine dioxide concentrations under comparable conditions. It is a logical conclusion that conditions for higher current densities, such as electrode blocking effects, lower electrode wetting and complicated geometries of the anode (extended mesh, edges, points, etc.) will also support the chlorine dioxide production. Risk can be reduced by applying low current loads (current densities) in technical apparatuses.
2. The chlorine dioxide formation is proportional to the chloride ion concentration. Significant influences of pH and rotation rate could not be found until now studying the electrochemical process.
3. The results indicate an electrochemical mechanism of ClO_2 production probably from chloride or active chlorine. Additionally, chemical mechanisms can be responsible for the chlorine dioxide formation, which has to be studied more in detail [129].

9.2. Electrodisinfection without by-products—possibility

The most popular form of ED is the E-C. The main advantage of this system is the on-site generation of disinfectants, thus avoiding the problems of common chlorination such as transport and storage of dangerous chlorine [12,133]. The E-C can be classified by two types [91]. One is to produce the mostly free chlorine from brine prepared for the electrolytic generator, and the other is to produce the oxidants directly [134] from the water to be treated through the electrolyser [135].

Only a few studies have been made to examine the disinfecting nature without generating chlorine. Kerwick et al. [91] showed that in the electrochemical cell containing a chloride-free sodium sulphate solution as electrolyte the disinfecting activity was maintained only during the electrolysis, whereas no residual effect was observed without applying current. They postulated that the short lived oxidants generated from the water discharge would be responsible for the inactivation. Guillou and El-Murr [136] also conducted the experiments in chloride-free phosphate buffer to inactivate *Saccharomyces cerevisiae*. It was just stated that the inactivation could not be attributed to the hydrogen peroxide, if any was present [135].

The Jeong et al. [135] study reported that in the ED using a Pt anode without generating chlorine the *E. coli* inactivation occurs through two distinct stages, which is characterised by the rapid inactivation at the beginning of electrolysis and the slower inactivation as the electrolysis proceeds further. These two stage inactivation is based on the separate mechanisms, involving the direct oxidation at electrode surface and the indirect oxidation mediated by hydroxyl radical. The results implicated that the ED could be successfully performed even without producing chlorine, demonstrating the potential application for disinfecting water that is not allow to contain any chloride ions (such as the production of sterilised ultra-pure water for the process of semiconductor cleaning).

10. Conclusion

From this review, the following conclusions can be drawn:

1. There is an increasing incidence in health problems related to environmental issues that originate from inadequate treatment of potable waters. This has compelled scientists and engineers to engage in innovative technologies to achieve a maximum disinfection at affordable costs. Some species of bacteria produce colonies and spores that can agglomerate in spherical clusters and thus protect organisms on the inside of the cluster against biocidal attack. Flocs of fine particles (e.g., clay) can entrap bacteria and this can also protect them against the biocides. Other bacteria have the ability to mutate, thus building up resistance to conventional biocides (e.g., chlorine).
2. The methods for water disinfection may be classified as follows: (1) chemical action: a variety of chemical agents (halogens and derivatives, oxygenated and highly oxidising compounds, metal ions) can be used to inactivate microorganisms; (2) physical action: electromagnetic radiation, particle radiation, and electrical current.
3. NOM, when measured as dissolved organic carbon (DOC), has levels in the range of 0.1–115 mg L^{-1}, with 5.75 mg L^{-1} reported as a global average for streams. The presence of NOM in source water adversely affects drinking water treatments and water quality of finished water. Apart from aesthetic problems of colour, taste and odour, NOM is well known to cause the potential hazard of DBP such as THMs and HAAs, the deterioration of water quality due to bacterial regrowth in distribution systems [21].
4. Much research has gone into factors underlying the formation and control of DBPs in water. This has spurred the search for alternative disinfectants to

chlorine and for advanced methods of DBP removal in treated water. Another viable THM control strategy is predicated on precursor removal prior to conventional disinfection practice.

5. Bacteria show a tendency to adsorb onto surfaces such as activated carbon, fibrous carbon, or ion exchange resins. This tendency is driven mainly by electrostatic forces between charged groups on the cell wall and on the adsorbent.
6. Several mechanisms have been proposed to account for the lethality of electrochemical exposure, including oxidative stress and cell death due to electrochemically generated oxidants ("killer" agents such as $^{\bullet}OH^{-}$), irreversible permeabilisation of cell membranes by the applied EF, and electrochemical oxidation of vital cellular constituents during exposure to electric current or induced EFs.
7. Laboratory experiments demonstrated that the ED process is highly effective for wastewater disinfection. According to the SEM investigation, E-C did not appear to be the predominant killing function during ED treatment. There were surface deformations observed for the *E. coli* cells after direct chlorination and ozonation. Some cell lysis could be recognised for the ozonated samples, which was not noticeable for the chlorinated samples. In contrast, substantial intracellular leakage was observed for the cells after ED as well as for the cells treated by the Fenton reaction. The similarity in the SEM morphology shared by the samples of ED and the radical process suggested that the germicidal action of ED was more close to the killing mechanism of hydroxyl radicals than that of chlorination. *E. coli* cells were apparently disinfected during the ED process by the chemical products with an oxidising power similar to that of hydroxyl free radicals and much stronger than that of chlorine. The SEM results support the hypothesis that the predominant killing function of ED is provided by high-energy intermediate products. Thus, in addition to E-C, the great capacity of ED is likely attributable to the generation of short-lived disinfectants, such as free radicals [69].
8. As compared with other chemical disinfection methods, the advantages of ED are obvious: no transport, storage and dosage of disinfectants are required. The disinfecting effect can be adjusted according to the on-site demand. ED shows a reservoir effect and is often more cost-effective and requires less maintenance than other disinfection methods. Photovoltaic power supply makes it possible to use ED far from the electrical supply grid. This may be important for its application to drinking water in developing countries. ED can also be used in conjunction with other disinfection methods.
9. EC as efficient process in mineral and organic matters removal has been proven also efficient in microorganisms (including *E. coli* and viruses) removal; hence, this electrochemical process may be presented as promising water treatment technology. However more studies must be done about the best choice of EC electrodes: anode in iron and cathode in metal that does not produce chlorine in water stream to avoid DBPs formation since it was eventually demonstrated that even at very low chloride concentrations (less than 100 mg L^{-1}) sufficient free chlorine can be produced to efficiently disinfect water [15].
10. Finally, technical cells should be designed and controlled better. The present state of non-controlled application of disinfection cells is not satisfying from hygienic and health risks points of view [129], i.e. more care should be taken to control inorganic DBP formation in order to avoid risks to the environment and human health when using electrodes of high oxidation power in solutions containing chloride [137].

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References

[1] J. Lohwacharin, K. Oguma and S. Takizawa, Effects of preadsorption by carbon black on membrane filtration of natural organic matter, Desalination Water Treat., 6 (2009) 74–79.

[2] C.A. Martínez-Huitle and E. Brillas, Electrochemical alternatives for drinking water disinfection, Angew. Chem. Int. Ed., 47 (2008) 1998–2005.

[3] A. Bennett, Drinking water: Pathogen removal from water – technologies and techniques, Filtration, Sep. 45 (2008) 14–16.

[4] N. Hankins, R. Price and N.A. Debacher, Process intensification during treatment of NOM-laden raw upland waters: Control and impact of the pre-coagulation regime during ultra-filtration, Desalination Water Treat., 8 (2009) 2–16.

[5] S.P. Chesters, E.G. Darton, S. Gallego and F.D. Vigo, The safe use of cationic flocculants with reverse osmosis membranes, Desalination Water Treat., 6 (2009) 144–151.

[6] F. Li, K. Wichmann and R. Otterpohl, Review of the technological approaches for grey water treatment and reuses, Sci. Total Environ., 407 (2009) 3439–3449.

[7] T. Ohtani, A. Kaneko, N. Fukuda, S. Hagiwara and S. Sase, Development of a membrane disinfection system for closed hydroponics in a greenhouse, J. Agric. Eng. Res., 77 (2000) 227–232.

[8] C. García, E. Rogel-Hernández, S.W. Lin and H. Espinoza-Gómez, Natural organic matter fouling using a cellulose acetate copolymer ultrafiltration membrane, Desalination Water Treat., 1 (2009) 150–156.

[9] E. Gaudichet-Maurin and F. Thominette, Ageing of polysulfone ultrafiltration membranes in contact with bleach solutions, J. Membr. Sci., 282 (2006) 198–204.

[10] J. de Koning, D. Bixio, A. Karabelas, M. Salgot and A. Schäfer, Characterisation and assessment of water treatment technologies for reuse, Desalination, 218 (2008) 92–104.

[11] B.H. Lee, W.C. Song, B. Manna and J.K. Ha, Dissolved ozone flotation (DOF)—a promising technology in municipal wastewater treatment, Desalination, 225 (2008) 260–273.

[12] K. Rajeshwar and J.G. Ibanez, Environmental electrochemistry: Fundamentals and applications in pollution sensors and abatement, Elsevier Sci. Technol. Books, 1997.

[13] C. Feng, K. Suzuki, S. Zhao, N. Sugiura, S. Shimada and T. Maekawa, Water disinfection by electrochemical treatment, Bioresour. Technol., 94 (2004) 21–25.

[14] Y. Delaedt, A. Daneels, P. Declerck, J. Behets, J. Ryckeboer, E. Peters and F. Ollevier, The impact of electrochemical disinfection on *Escherichia coli* and *Legionella pneumophila* in tap water, Microbiol. Res., 163 (2008) 192–199.

[15] A. Kraft, Electrochemical water disinfection: A short review, electrodes using platinum group metal oxides, Platinum Metals Rev., 52 (2008) 177–185.

[16] H. Bergmann, T. Iourtchouk, K. Schöps and K. Bouzek, New UV irradiation and direct electrolysis—promising methods for water disinfection, Chem. Eng. J., 85 (2002) 111–117.

[17] Q. Xiangli, Z. Zhenjia, W. Nongcun, V. Wee, M. Low, C.S. Loh and N.T. Hing, Coagulation pretreatment for a large-scale ultrafiltration process treating water from the Taihu River, Desalination, 230 (2008) 305–313.

[18] F. Ge, L. Zhu, J. Wang, Distribution of chlorination products of phenols under various pHs in water disinfection, Desalination, 225 (2008) 156–166.

[19] G.V. Korshin and M.D. Jensen, Electrochemical reduction of haloacetic acids and exploration of their removal by electrochemical treatment, Electrochim. Acta 47 (2001) 747–751.

[20] M. Belkacem, K. Bensadok, A. Refes, P.M. Charvier and G. Nezzal, Water produce for pharmaceutical industry: role of reverse osmosis stage, Desalination, 221 (2008) 298–302.

[21] J.-Y. Tian, H. Liang, X. Li, S.-J. You, S. Tian and G.-B. Li, Membrane coagulation bioreactor (MCBR) for drinking water treatment, Water Res., 42 (2008) 3910–3920.

[22] S. Abderrahmane, A. Himour and L. Ponsonnet, Inactivation of *E. coli* and *Pseudomonas aeruginosa* by electrochloration under bipolar pulsed polarization, Materials Sci. Eng. C 28 (2008) 901–905.

[23] K. Vijayaraghavan, D. Ahmad and A.Y.A. Yazid, Electrolytic treatment of latex wastewater, Desalination, 219 (2008) 214–221.

[24] S. Hong, S. Kim and C. Bae, Efficiency of enhanced coagulation for removal of NOM and for adsorbability of NOM on GAC, Desalination Water Treat., 2 (2009) 89–94.

[25] M.M. Donnermair and E.R. Blatchley III, Disinfection efficacy of organic chloramines, Water Res., 37 (2003) 1557–1570.

[26] P.C. Singer, Control of disinfection by-products in drinking water, J. Environ. Eng.—ASCE, 120 (1994) 727–744.

[27] USEPA, Stage 2 disinfectants and disinfection byproducts Rule, EPA-HQ-OW (2006) 2002–0043.

[28] G. Hua and D.A. Reckhow, Comparison of disinfection byproduct formation from chlorine and alternative disinfectants, Water Res., 41 (2007) 1667–1678.

[29] C.J. Seidel, M.J. McGuire, R.S. Summers and S. Via, Have utilities switched to chloramines? J. AWWA, 97 (2005) 87–97.

[30] A.C. Diehl, G.E. Speitel, J.M. Symons, S.W. Krasner, C.J. Hwang and S.E. Barrett, DBP formation during chloramination, J. AWWA, 92 (2000) 76–90.

[31] D.A. Reckhow and P.C. Singer, The removal of organic halide precursors by preozonation and alum coagulation, J. AWWA, 76 (1984) 151–157.

[32] J. Hoigne and H. Bader, The formation of trichloronitromethane (chloropicrin) and chloroform in a combined ozonation/chlorination treatment of drinking water, Water Res., 3 (1988) 313–319.

[33] J.G. Jacangelo, N.L. Patania, K.M. Reagen, E.M. Aieta, S.W. Krasner and M.J. McGuire, Ozonation: assessing its role in the formation and control of disinfection by-products, J. AWWA, 81 (1989) 74–84.

[34] V. Kochkodan, S. Tsarenko, N. Potapchenko, V. Kosinova and V. Goncharuk, Adhesion of microorganisms to polymer membranes: a photobactericidal effect of surface treatment with TiO_2, Desalination, 220 (2008) 380–385.

[35] E.M. Aieta and J.D. Berg, A review of chlorine dioxide in drinking water treatment, J. AWWA, 78 (1986) 62–72.

[36] K.S. Werdehoff and P.C. Singer, Chlorine dioxide effects on THMFP, TOXFP and the formation of inorganic by-products, J. AWWA, 79 (1987) 107–113.

[37] E. Joyce, T.J. Mason, S.S. Phull and J.P. Lorimer, The development and evaluation of electrolysis in conjunction with power ultrasound for the disinfection of bacterial suspensions, Ultrasonics Sonochem., 10 (2003) 231–234.

[38] D. Ghernaout, B. Ghernaout, A. Saiba, A. Boucherit and A. Kellil, Removal of humic acids by continuous electromagnetic treatment followed by electrocoagulation in batch using aluminium electrodes, Desalination, 239 (2009) 295–308.

[39] D. Ghernaout, A. Badis, A. Kellil and B. Ghernaout, Application of electrocoagulation in *Escherichia coli* culture and two surface waters, Desalination, 219 (2008) 118–125.

[40] K.-H. Choo and S.-K. Kang, Removal of residual organic matter from secondary effluent by iron oxides adsorption, Desalination 154 (2003) 139–146.

[41] T. Matsunaga, M. Okochi, M. Takahashi, T. Nakayama, H. Wake and N. Nakamura, TiN electrode reactor for disinfection of drinking water, Water Res.34 (2000) 3117–3122.

[42] A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, R. Pompei and S. Laconi, Characterisation of a stirred tank electrochemical cell for water disinfection processes, Electrochim. Acta52 (2007) 2595–2602.

[43] G. Ciardelli and N. Ranieri, The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation, Water Res.35 (2001) 567–572.

[44] D. E. Kimbrough and I.H. Suffet, Electrochemical removal of bromide and reduction of THM formation potential in drinking water, Water Res.36 (2002) 4902–4906.

[45] J.-Q. Jiang and B. Lloyd, Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Res.36 (2002) 1397–1408.

[46] P.A. Christensen, T.P. Curtis, T.A. Egerton, S.A.M. Kosa and J.R. Tinlin, Photoelectrocatalytic and photocatalytic disinfection of *E. coli* suspensions by titanium dioxide, Appl. Catal. B: Environ.41 (2003) 371–386.

[47] P. Drogui, S. Elmaleh, M. Rumeau, C. Bernard and A. Rambaud, Hybride process, microfiltration-electroperoxidation, for water treatment, J. Membr. Sci.186 (2001) 123–132.

[48] D. Gášková, K. Sigler, B. Janderová and J. Plášek, Effect of high-voltage electric pulses on yeast cells: factors influencing the killing efficiency, Bioelectrochem. Bioener.39 (1996) 195–202.

[49] K.P. Drees, M. Abbaszadegan and R.M. Maier, Comparative electrochemical inactivation of bacteria and bacteriophage, Water Res.37 (2003) 2291–2300.

[50] J.C. Weaver and Y.A. Chizmadzhev, Theory of electroporation: A review, Bioelectrochem. Bioener. 41 (1996) 135–160.

[51] T. Matsunaga, S. Naksono, T. Takamuku, J.G. Burgess, N. Nakamura and K. Sode, Disinfection of drinking water by using a novel electrochemical reactor employing carbon-cloth electrodes, Appl. Environ. Microbiol.,58 (1992) 686–689.

[52] G. Patermarakis and E. Fountoukidis, Disinfection of water by electrochemical treatment, Water Res., 24 (1990)1491–1496.

[53] H. Tokuda and K. Nakanishi, Application of direct current to protect bioreactor against contamination, Biosci. Biotechnol. Biochem., 59 (1995) 753–755.

[54] M. Okochi, N. Nakamura and T. Matsunaga, Electrochemical killing of microorganisms using the oxidized form of ferrocenemonocarboxylic acid, Electrochim. Acta, 44 (1999) 3795–3799.

[55] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.

[56] H. Särkkä, M. Vepsäläinen, M. Pulliainen and M. Sillanpää, Electrochemical inactivation of paper mill bacteria with mixed metal oxide electrode, J. Hazard. Mater., 156 (2008) 208–213.

[57] K.V. Radha, V. Sridevi, K. Kalaivani and M. Raj, Electrochemical decolorization of the dye Acid orange 10, Desalination Water Treat., 7 (2009) 6–11.

[58] S. Vasudevan, J. Lakshmi, J. Jayaraj and G. Sozhan, Remediation of phosphate-contaminated water by electrocoagulation with aluminium, aluminium alloy and mild steel anodes, J. Hazard. Mater., 164 (2009) 1480–1486.

[59] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras and D. Mantzavinos, Electrochemical oxidation of olive oil mill wastewaters, Water Res. 39 (2005) 4177–4187.

[60] M. Tir and N. Moulai-Mostefa, Electrochemical treatment of metal working emulsions using Box-Behnken design, Desalination Water Treat., 7 (2009) 214–219.

[61] A. Khelifa, S. Moulay, F. Hannane, S. Benslimene and M. Hecini, Application of an experimental design method to study the performance of electrochlorination cells, Desalination, 160 (2004) 9 l–98.

[62] J. Jeong, J.Y. Kim and J. Yoon, The role of reactive oxygen species in the electrochemical inactivation of microorganisms, Environ. Sci. Technol. 40 (2006) 6117–6122.

[63] C. Flox, J.A. Garrido, R.M. Rodriquez, F. Centellas, P.-L. Cabot, C. Arias and E. Brillas, Degradation of 4,6-dinitro-*o*-cresol from water by anodic oxidation with a boron-doped diamond electrode, Electrochim. Acta, 50 (2005) 3685–3692.

[64] W. Liang, J. Qu, L. Chen, H. Liu and P. Lei, Inactivation of *Microcystis aeruginosa* by continuous electrochemical cycling process in tube using Ti/RuO_2 electrodes, Environ. Sci. Technol., 39 (2005) 4633–4639.

[65] H.S. Awad and N. Abo Galwa, Electrochemical degradation of acid blue and basic brown dyes on Pb/PbO_2 electrode in the presence of different conductive electrolyte and effect of various operating factors, Chemosphere, 61 (2005) 1327–1335.

[66] M.E.H. Bergmann and A.S. Koparal, Studies on electrochemical disinfectant production using anodes containing RuO_2, J. Appl. Electrochem., 35 (2005) 1321–1329.

[67] J. Wang and J. Farrell, Electrochemical inactivation of triclosan with boron doped diamond film electrodes, Environ. Sci. Technol., 38 (2004) 5232–5237.

[68] J.C. Mierzwa, I. Hespanhol, M.C.C. da Silva, L.D.B. Rodrigues and C.F. Giorgi, Direct drinking water treatment by spiral-wound ultrafiltration membranes, Desalination, 230 (2008) 41–50.

[69] H.F. Diao, X.Y. Li, J.D. Gu, H.C. Shi and Z.M. Xie, Electron microscopic investigation of the bactericidal action of electrochemical disinfection in comparison with chlorination, ozonation and Fenton reaction, Process Biochem. 39 (2004) 1421–1426.

[70] G.C. White, Handbook of chlorination and alternative disinfectants, 4th ed., Wiley, 1999.

[71] R.J. Aitken, J.S. Clarkson and S. Fishel, Generation of reactive oxygen species, lipid peroxidation, and human sperm function, Biol. Reprod. 41 (1989) 183–197.

[72] X.Y. Li, F. Ding, P.S.Y. Lo and S.H.P. Sin, Electrochemical disinfection of saline wastewater effluent, J. Environ. Eng., ASCE 128 (2002) 697–704.

[73] G.E. Stoner and G.L. Cahen, The mechanism of low frequency AC electrochemical disinfection, Bioelectrochem. Bioeng. 9 (1982) 229–243.

[74] P. Natishan, The use of composite electrodes for the electrochemical disinfection of recirculating fluids, Ph.D. dissertation, Charlottesville, VA, USA, University of Virginia, 1984.

[75] T. Grahl and H. Markl, Killing of microorganisms by pulse electric fields, Appl. Microbiol. Biotechnol., 45 (1996) 148–157.

[76] T. Matsunaga, S. Nakasono, Y. Kitajima and K. Horiguchi, Electrochemical disinfection of bacteria in drinking water using activated carbon fibers, Biotechnol. Bioeng., 43 (1994) 429–433.

[77] H. Shinohara, J. Kojima, M. Yaoita and M. Aizawa, Electrically stimulated rupture of cell membranes with a conducting polymer-coated electrode, Bioelectrochem. Bioeng., 22 (1989) 23–35.

[78] A. Kraft, Electrochemical water disinfection. Part I. Hypochlorite production from very dilute chloride solutions, J. Appl. Electrochem., 29 (1999) 861–868.

[79] S.K. Johnson, L.L. Houk, J.R. Feng, R.S. Houk and D.C. Johnson, Electrochemical incineration of 4-chlorophenol and identification of products and intermediates by mass spectrometry, Environ. Sci. Technol., 33 (1999) 2638–2644.

[80] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: application to herbicide 2,4-D, J. Appl. Electrochem., 30 (2000) 475–482.

[81] M. Saran, I. Beck-Speier, B. Fellerhoff and G. Bauer, Phagocytic killing of microorganisms by radical processes: consequences of the reaction of hydroxyl radicals with chloride yielding chlorine atoms, Free Radic. Biol. Med., 26 (1999) 482–490.

[82] M.J. Rodriguez, J.-B. Sérodes and P. Levallois, Behavior of trihalomethanes and haloacetic acids in a drinking water distribution system, Water Res., 38 (2004) 4367–4382.

[83] J.J. Rook, Formation of haloforms during chlorination of nature water, J. Water Treat. Exam., 23 (1974) 234–243.

[84] E.R. Blatchley III, D. Margetas and R. Duggirala, Copper catalysis in chloroform formation during water chlorination, Water Res., 37 (2003) 4385–4394.

[85] L. Zhi-sheng, Y. Jun, L. Li and Y. Yu-juan, Characterization of NOM and THM formation potential in reservoir source water, Desalination Water Treat., 6 (2009) 1–4.

[86] S.A. Alizadeh Tabatabai, M.D. Kennedy, G.L. Amy and J.C. Schippers, Optimizing inline coagulation to reduce chemical consumption in MF/UF systems, Desalination Water Treat., 6 (2009) 94–101.

[87] M. Tomaszewska, S. Mozia and A.W. Morawski, Removal of organic matter by coagulation enhanced with adsorption on PAC, Desalination, 161 (2004) 79–87.

[88] I. Galambos, G. Vatai and E. Belkássy-Molnár, Membrane screening for humic substances removal, Desalination, 162 (2004) 111–116.

[89] V. Uyak and I. Toroz, Disinfection by-product precursors reduction by various coagulation techniques in Istanbul water supplies, J. Hazard. Mater., 141 (2007) 320–328.

[90] F.X.R. Van Leeuwen, Safe drinking water: the toxicologist's approach, Food Chem. Toxicol., 38 (2000) S51–S58.

[91] M.I. Kerwick, S.M. Reddy, A.H.L. Chamberlain and D.M. Holt, Electrochemical disinfection, an environmentally acceptable method of drinking water disinfection? Electrochim. Acta, 50 (2005) 5270–5277.

[92] C.A. Martínez-Huitle and E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review, Appl. Catal. B: Environ., 87 (2009) 105–145.

[93] G. Horner and J.G. Duffey, Electrochemical removal of heavy metals from waste water, The American Electroplaters Society Annual Meeting, Denver, CO, 1983.

[94] C. Tsouris, D.W. DePaoli, J.T. Shor, M. Hu and T.-Y. Ying, Electrocoagulation for magnetic seeding of colloidal particles, Colloids Surf. A: Physicochem. Eng. Aspects, 177 (2001) 223–233.

[95] O.T. Can, M. Bayramoglu and M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, Ind. Eng. Chem. Res., 42 (2003) 3391–3396.

[96] D. Mills, A new process for electrocoagulation, J. AWWA, 92 (2000) 34–43.

[97] J.-W. Feng, Y.-B. Sun, Z. Zheng, J.-B. Zhang, S. Li and Y.-C. Tian, Treatment of tannery wastewater by electrocoagulation, J. Environ. Sci., 19 (2007) 1409–1415.

[98] N. Shirasaki, T. Matsushita, Y. Matsui, M. Kobuke and K. Ohno, Comparison of removal performance of two surrogates for pathogenic waterborne viruses, bacteriophage Q and MS2, in a coagulation–ceramic microfiltration system, J. Membr. Sci., 326 (2009) 564–571.

[99] B. Zhu and D.A. Clifford, S. Chellam, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes, Water Res., 39 (2005) 3098–3108.

[100] G. Roa-Morales, E. Campos-Medina, J. Aguilera-Cotero, B. Bilyeu and C. Barrera-Díaz, Aluminum electrocoagulation with peroxide applied to wastewater from pasta and cookie processing, Sep. Purif. Technol. 54 (2007) 124–129.

[101] M.Y.A. Mollah, R. Schennach, J.R. Parga and D.L. Cocke, Electrocoagulation (EC)—science and application, J. Hazard. Mater., B84 (2001) 29–41.

[102] K. Yetilmezsoy, F. Ilhan, Z. Sapci-Zengin, S. Sakar and M.T. Gonullu, Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: A post-treatment study, J. Hazard. Mater., 162 (2009) 120–132.

[103] J.Q. Jiang, Research progress in the use of ferrate(VI) for the environmental remediation, J. Hazard. Mater., 146 (2007) 617–623.

[104] V. Lescuras-Darrou, F. Lapicque and G. Valentin, Electrochemical ferrate generation for waste water treatment using cast irons with high silicon contents, J. Appl. Electrochem., 32 (2002) 57–63.

[105] P. Cañizares, M. Arcís, C. Sáez and M.A. Rodrigo, Electrochemical synthesis of ferrate using boron doped diamond anodes, Electrochem. Commun., 9 (2007) 2286–2290.

[106] M. Alsheyab, J.-Q. Jiang and C. Stanford, On-line production of ferrate with an electrochemical method and its potential application for wastewater treatment – A review, J. Environ. Manag., 90 (2009) 1350–1356.

[107] V.K. Sharma, Potassium ferrate (VI): an environmentally friendly oxidant, Adv. Environ. Res., 6 (2002) 143–156.

[108] Y. Lee, I.H. Um and J. Yoon, Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation, Environ. Sci. Technol. 37 (2004) 5750–5756.

[109] D. Tiwari, J.Q. Yang and S.M. Lee, Application of ferrate(VI) in the treatment of wastewaters, Environ. Eng. Res. 10 (2005) 269–282.

[110] S. Licht and X. Yu, Recent advances in Fe(VI) synthesis (ch. 1), In: Ferrates, synthesis, properties, and applications in water and wastewater treatment, V.K. Sharma (Ed.), ACS Symposium Series; American Chemical Society, Washington, DC, 2008.

[111] C. Zhang, Z. Liu, F. Wu, L. Lin and F. Qi, Electrochemical generation of ferrate on SnO_2–Sb_2O_3/Ti electrodes in strong concentration basic condition, Electrochem. Commun.6 (2004) 1104–1109.

[112] J. Híveš, M. Benová, K. Bouzek and V.K. Sharma, Electrochemical formation of ferrate(VI) in a molten NaOH–KOH system, Electrochem. Commun. 8 (2006) 1737–1740.

[113] Z. Mácová, K. Bouzek and V.K. Sharma, The role of the electrode and electrolyte composition in the anode dissolution kinetics, Comparison of the ferrate(VI) synthesis in the solutions of NaOH and KOH of various ratio (ch. 2), In: Ferrates, synthesis, properties, and applications in water and wastewater treatment, V.K. Sharma (Ed.), ACS Symposium Series; American Chemical Society, Washington, DC, 2008.

[114] M. Benová, J. Híveš, K. Bouzek and V.K. Sharma, Electrochemical ferrate(VI) synthesis: A molten salt approach (ch. 3), In: Ferrates, synthesis, properties, and applications in water and wastewater treatment, V.K. Sharma (Ed.), ACS Symposium Series; American Chemical Society: Washington, DC, 2008.

[115] F. Lapicque and G. Valentin, Direct electrochemical preparation of solid potassium ferrate, Electrochem. Commun.4 (2002) 764–766.

[116] J.-Q. Jiang, C. Stanford and M. Alsheyab, The online generation and application of ferrate(VI) for sewage treatment—A pilot scale trial, Sep. Purif. Technol.68 (2009) 227–231.

[117] Z. Mácová, K. Bouzek, J. Híveš, V.K. Sharma, R.J. Terryn and J.C. Baum, Research progress in the electrochemical synthesis of ferrate(VI), Electrochim. Acta54 (2009) 2673–2683.

[118] N.V. Nikolaev, A.S. Kozlovsii and I.I. Utkin, Treating natural waters in small water systems by filtration with electrocoagulation, Soviet J. Water Chem. Technol. 4 (1983) 70–73.

[119] E.A. Vik, D.A. Carlson, A.S. Eikum and E.T. Gjessing, Electrocoagulation of potable water, Water Res. 18 (1984) 1355–1360.

[120] G.A. Ciorba, C. Radovan, I. Vlaicu and S. Masu, Removal of nonylphenol ethoxylates by electrochemically-generated coagulants, J. Appl. Electrochem. 32 (2002) 561–567.

[121] M.E. Pulido, E.J. Lamotta and R.M.J. Nandipati, Field-scale demonstration of electrocoagulation and enhanced media filtration for treatment of shipyard storm water, J. Ship Production,17 (2001) 191–201.

[122] P.K. Holt, G.W. Barton, M. Wark and C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloid Surf. A., 211 (2002) 233–248.

[123] M. Han, A. Kwon, Preliminary investigation of electrocoagulation as a substitute for chemical coagulation, Water Sci. Technol.: Water Supply, 2 (2002) 73–76.

[124] N.S. Abuzaid, A.A. Bukhari and Z.M. Hamouz, Ground water coagulation using soluble stainless steel electrodes, Adv. Environ. Res., 6 (2002) 325–333.

[125] Y. Xu, J.-Q. Jiang, K. Quill, J. Simon and K. Shettle, Electrocoagulation: a new approach for the removal of boron containing wastes, Desalination Water Treat., 2 (2009) 131–138.

[126] M.M. Emamjomeh and M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manag., 90 (2009) 1663–1679.

[127] D. Ghernaout, B. Ghernaout and A. Kellil, Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation, Desalination Water Treat., 2 (2009) 203–222.

[128] D. Ghernaout, B. Ghernaout, A. Boucherit, M.W. Naceur, A. Khelifa and A. Kellil, Study on mechanism of electrocoagulation with iron electrodes in idealised conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes, Desalination Water Treat., 8 (2009) 91–99.

[129] H. Bergmann and S. Koparal, The formation of chlorine dioxide in the electrochemical treatment of drinking water for disinfection, Electrochim. Acta, 50 (2005) 5218–5228.

[130] D.J. Fisher, D.T. Burton, L.T. Yonkos, S.D. Turley, G.P. Ziegler and B.S. Turley, Derivation of acute ecological risk criteria for chlorite in freshwater ecosystems, Water Res., 37 (2003) 4359–4368.

[131] R.A. Minear and G.L. Amy, Disinfection by-products in water treatment, in: The Chemistry of their Formation and Control, Lewis Publishers, Boca Raton, FL, 1996.

[132] H. Junli, W. Li, R. Nenqi, L.X. Li, S.R. Fun and Y. Guanle, Disinfection effect of chlorine dioxide on viruses, algae and animal planktons in water, Water Res., 31 (1997) 455–460.

[133] Y. Xu, J. Yang, M. Ou, Y. Wang and J. Jia, Study of *Microcystis aeruginosa* inhibition by electrochemical method, Biochem. Eng. J., 36 (2007) 215–220.

[134] H. Bergmann, A.T. Koparal, A.S. Koparal and F. Ehrig, The influence of products and by-products obtained by drinking water electrolysis on microorganisms, Microchem. J., 89 (2008) 98–107.

[135] J. Jeong, J.Y. Kim, M. Cho, W. Choi and J. Yoon, Inactivation of *Escherichia coli* in the electrochemical disinfection process using a Pt anode, Chemosphere, 67 (2007) 652–659.

[136] S. Guillou and N. El-Murr, Inactivation of *Saccharomyces cerevisiae* in solution by low-amperage electric treatment, J. Appl. Microbiol., 92 (2002) 860–865.

[137] M.E.H. Bergmann, J. Rollin and T. Iourtchouk, The occurrence of perchlorate during drinking water electrolysis using BDD anodes, Electrochim. Acta, 54 (2009) 2102–2107.